Cobalt Sulfide-Based Composite Material for Photocatalysis

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Photocatalysis, as an inexpensive and safe technology to convert solar energy, is essential for the efficient utilization of sustainable renewable energy sources. Earth-abundant cobalt sulfide-based composites have generated great interest in the field of solar fuel conversion because of their cheap, diverse structures and facile preparation.

photocatalysis cobalt sulfide synthesis strategies

1. Photocatalytic H_2 Production

Semiconductor photocatalytic water decomposition has been improved by integrating appropriate co-catalysts. Due to the sufficient catalytic site and easy preparation, cobalt sulfide-based cocatalysts have been widely applied as co-catalysts for various semiconductors toward photocatalytic hydrogen evolution [1][2][3][4]. Fu et al. have illustrated that combining a hollow cobalt sulfide (CoS_x) polyhedral cocatalyst with g-C_3N_4 can effectively accelerate the separation of photoinduced charges in g-C_3N_4 and provide an abundant active site to promote redox reactions [5]. In addition, the hollow structure of the CoS_x polyhedron can also allow multiple reflections of light to enhance the light collection of g-C_3N_4. Thus, the photocatalytic performance of the 2% CoS_x/g-C_3N_4 hybrids was significantly better than that of the blank g-C_3N_4. Obviously, the incorporation of cobalt sulfide could act as a cocatalyst to accelerate the separation and transfer of photo-generated electron-hole pairs and reduce the overpotential of the hydrogen production reaction. Qiu et al. reported that CdS nanorods loaded with CoS_2 nanoparticles exhibited excellent photocatalytic hydrogen production activity, which was 13 times higher than that of pristine CdS NRs samples, and the optimized CoS_2/CdS NRs photocatalyst had high stability and recyclability [6].

In addition to the cobalt sulfide single component cocatalyst, multicomponent cocatalysts exhibit superior co-catalytic activity than single component cocatalysts. For example, Li et al. have reported an excellent composite photocatalyst by combining CoS with $Co(OH)_2$ on g-C_3N_4 to construct a dual cocatalyst [7]. The photocatalytic hydrogen production rate of the CoS/Co $(OH)_2$/g-C_3N_4 composite photocatalyst is 311 times higher than that of pure g-C_3N_4, which is due to the synergistic effect of the dual cocatalysts. In the dual cocatalyst system, CoS cocatalyst acts as an electron acceptor to facilitate the separation of photogenerated carriers, and $Co(OH)_2$ can also act as a conductor to diffuse photon-generated electrons. Moreover, in addition to acting as a co-catalyst, cobalt sulfide has also been reported as a semiconductor for H_2 production. For example, Zhang et al. used a simple hydrothermal synthesis method to in situ grow two-dimensional $ZnIn_2S_4$ on one-dimensional hollow Co_9S_8

nanotubes to form a $Co_9S_8/ZnIn_2S_4$ heterostructure [8]. Type-I heterostructures are constructed when the Co_9S_8 nanotubes are covered with $ZnIn_2S_4$ nanosheets. When the $Co_9S_8/ZnIn_2S_4$ composites are excited to generate electron-hole pairs, the photogenerated electrons can migrate rapidly from the CB of $ZnIn_2S_4$ to that of Co_9S_8. Consequently, the $Co_9S_8/ZnIn_2S_4$ heterostructure achieves a higher photocatalytic activity than pure $ZnIn_2S_4$.

2. Photocatalytic CO_2 Reduction

In addition to being used as a cocatalyst for photocatalytic H_2 production, cobalt sulfide can also be used as efficient photocatalytic for CO_2 reduction [9][10]. For example, Zhang et al. have composited the hollow Co_9S_8 nanocages with $ZnIn_2S_4$ nanosheets and CdS quantum dots to construct a ternary composite photocatalyst [11]. The hollow structure of Co_9S_8 nanocages promotes multiple reflections of sunlight in the cavity, which enhanced the light absorption of $ZnIn_2S_4$ nanosheets and CdS quantum dots. In addition,, the ternary composite photocatalyst form a double Z-type heterojunction, which facilitates the separation and migration of photogenic electron hole pairs. Therefore, the photocatalytic performance of the Co_9S_8@$ZnIn_2S_4$/CdS hybrid is obviously better than that of blank CdS and $ZnIn_2S_4$.

Moreover, photocatalytic reduction of CO_2 to methanol is another ideal approach for solar energy conversion. Ma et al. have prepared carbon nitride (CN) loaded with cobalt sulfide (CS) as a cocatalyst. The optimized CS/CN photocatalyst was 2.3 times more selective for CH_3OH than CN [12]. It was confirmed that the introduction of cobalt sulfide can improve the selectivity of CH_3OH. The cobalt sulfide not only provides the H_2O oxidation center but also can significantly weaken the overpotential of the H_2O oxidation half reaction, thus effectively avoiding the formation of strongly oxidized radicals.

Furthermore, Wang et al. have reported hierarchical $FeCoS_2$-CoS_2 double-shelled nanotubes as a composite photocatalyst for CO_2 reduction [13]. $FeCoS_2$-CoS_2 composites can be obtained after ion-exchange reactions and sulfidation reactions with MIL-88A as precursors. $FeCoS_2$-CoS_2 composites present a uniform hierarchical nanosheet structure. When the $Ru(bpy)_3^{2+}$ is used as the photosensitizer, the optimal $FeCoS_2$-CoS_2 composite shows excellent photocatalytic activity with a CO generation rate of 28.1 μmol h^{-1}, which is better than the individuals of $FeCoS_2$ and CoS_2 and their physical mixtures sample. The unique hierarchical nanosheet structure reduces diffusion length and enhances scattering in the cavity, which inhibits electron-hole recombination and exposes active sites for redox reactions, thus improving the photocatalytic activity of the $FeCoS_2$-CoS_2 composite.

3. Photocatalytic Nitrogen Fixation

Neither humans nor the earth's ecosystem can survive without the ability to synthesize ammonia [14]. The production of this foundation sustaining life on earth is based on both industrial and biological fixation levels of 200 × 10^6 tons per year [15]. At present, nitrogen fixation is principally carried out in three ways: (i) biological nitrogen fixation. Some micro-organisms, such as nitrogen-fixing bacteria, use their own nitrogenase to fix N_2 molecules for biological nitrogen fixation; (ii) high-energy nitrogen fixation in geochemical processes, such as lightning; (iii) the

energy-intensive Haber–Bosch method for industrial nitrogen fixation. However, biological and geochemical nitrogen fixation solely account for a tiny fraction of the fixed nitrogen supply. The Haber–Bosch process, which uses N_2 and H_2 as sources and iron-based compounds as the main material, is currently the main route for the synthesis of industrial ammonia. Nevertheless, this process requires a great deal of energy input while generating large emissions of by-products (such as carbon dioxide), which may cause environmental hazards. Hence, developing high-selectivity photocatalysts for nitrogen-reducing ammonia is challenging and interesting research [15]. Recently, Yuan et al. have demonstrated that loading Ru/CoS_x to g-C_3N_4 nanosheets can effectively activate N_2 molecules and facilitate the separation of light-induced electron-hole pairs in g-C_3N_4 [16]. In comparison with pure CN, Ru-Vs-CoS/CN shows obviously enhanced photocatalytic activity, reaching 1.28% apparent quantum efficiency at 400 nm and 0.042% solar-to-ammonia efficiency. The excellent nitrogen reduction reaction performance is attributed to the fact that the sulfur vacancies in CoS_x can effectively promote the selective chemisorption of N_2 molecules. In addition, an N_2 molecule is bridged against the side-on Ru-Co center by the undercoordination of Ru and Co atoms at the Ru/CoS_x interface. Furthermore, the plasmonic Ru/CoS_x interface enhances light absorption to generate energetic charge-carriers, accelerates charge separation and transfer, and therefore kinetically facilitates the fixation of N_2. This confirms that the presence of vacancies on the surface of cobalt sulfide-based nanomaterials exhibits excellent photocatalytic NRR performance, as it can modify the electronic structure, decrease the coordination number of surface atoms, facilitate the formation of dangling bonds, and greatly promote the formation of N_2 chemisorption and activation. The N_2-fixation mechanism indicates the hydrogen evolution reaction (HER) on Ru occurs easily due to its good free energy of hydrogen production (−0.07 eV). Meanwhile, the active hydrogen adsorption on Co and desorption on S limit the hydrogen evolution reaction (HER) on Ru.

4. Photocatalytic Degradation

Recent research shows that cobalt sulfide-based materials, such as CoS, CoS_2, and Co_3S_4, are important candidate catalysts for photocatalytic organic pollutants degradation [17][18][19][20]. For instance, $Co_{2.67}S_4$ shows excellent photocatalytic degradation efficiency of methylene blue (MB) under UV, visible, and near-infrared irradiation [21]. The valence state change of cobalt ions effectively separates electrons from holes and accelerates electron transfer, thus enhancing the activity of photocatalytic degradation. In addition to single cobalt-based sulfide materials, cobalt sulfide, as a co-catalyst, can be combined with host semiconductors for photocatalytic degradation. For example, Tang et al. have designed a two-dimensional CoS/BiOBr heterojunction, which shows a 5.3-fold higher degradation rate as compared to pure BiOBr [22]. When the BiOBr and the CoS combine to construct the CoS/BiOBr heterojunction photocatalyst, the electrons on the CB of the CoS can be easily transferred to the CB of the BiOBr. In addition, the VB of BiOBr can oxidize glyphosate directly, producing small molecules or ions (PO_4^{3-}, etc.). Simultaneously, some holes also migrate from BiOBr to CoS, leading to effective photogenerated charge carrier separation and thereby boosting the photocatalytic performance of the CoS/BiOBr composite.

Moreover, Zhang et al. have covered uniformly MoS_2 nanosheets on CoS_2 nanoparticles to construct CoS_2/MoS_2-nitrogen-doped graphene aerogels for photocatalytic organic pollutants degradation [23]. When MoS_2 is combined with CoS_2, the band gap of MoS_2 can be narrowed and the optical response range can be expanded. At the same time, CoS_2 can effectively accelerate the charge separation and increase the surface-active sites. Taking advantage of these advantages, the optimized three-dimensional CoS_2/MoS_2-nitrogen-doped graphene aerogel photocatalyst can degrade pollutants up to 97.1% within 60 minimums and still maintain 95.1% after three cycles.

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